TEMPLATE

The present invention relates to a template for use in the manufacture of structures on the nanometre scale.

5   The provision of templates for use in the production of structures on the nanometre scale and, in particular, the provision of templates to produce very detailed and intricately patterned structures is very difficult.

According to the present invention, a template is
10   provided which is formed from a layered structure comprising a substrate and a single-phase polymer layer positioned on the substrate, wherein the polymer layer comprises a textured surface, the texturing being caused by induction of stress in the polymer layer.

15   According to the present invention, a method of manufacture of a structure on the nanometre scale comprises the steps of providing a template as defined above, molding a material on to the template and removing the molded material from the template to provide the desired
20   structure.

According to the present invention, a method of making a template comprises the steps of depositing a layer of a single-phase polymer on to a substrate, baking the resulting structure from the deposition step at a
25   temperature below the glass transition temperature (T_g) of the single-phase polymer, texturing a surface of the polymer layer by inducing stress in the polymer layer and annealing the resulting structure from the stress-induction step to provide a template.

30   The present invention therefore surprisingly utilises the fine structures generated by topographic instabilities in single-phase polymer films, and thus enables the production of highly intricate, organised structures on the nanometre scale, so-called "nanostructures".

35   The method of making a template according to the present invention provides a simple, fast and effective way of producing a template, which may then be used in the

production of nanostructures for use in a variety of applications. Patterning of the template may be controlled by optimisation of the fabrication parameters, for example the temperature or polymer film thickness employed.

5   The template of the invention may be used in the manufacture of a variety of nanostructures such as arrays, grids and electronic or optical devices such as polarisers. Such structures have many applications not only in the fields of optics and electronics but also, for instance, in

10   molecular separation techniques, for example the separation of DNA. Also, unlike processes which involve the use of patterned substrates, the method of manufacture of the invention does not employ lithography and therefore provides a new avenue for the fabrication of

15   nanostructures.

The substrate comprised in the template of the invention is preferably inorganic and more preferably comprises silicon. The thickness of the substrate will typically be approximately 0.5 mm.

20   Any single-phase polymer may be comprised in the template of invention, however, the single-phase polymer is preferably selected from polymethylglutarimide (PMGI), polymethylmethacrylate (PMMA) and photoresists, such as AZ5214E, which is manufactured by Clarland GmbH and

25   comprises 2-methoxy-1-methylethylacetate as its main component. More preferably, the single-phase polymer is PMGI. The thickness of the single-phase polymer layer may vary depending on the intricacy of the desired texturing or patterning of the template, however, it is typically in the

30   range 50-300 nm.

The template may additionally comprise a thin, rigid layer comprising a semiconductor or a metal for example. This layer is positioned on the single-phase polymer layer and will typically have a thickness of approximately 10 nm.

35   If the template comprises a semiconductor layer, the semiconductor will preferably be germanium, which is favourable for further pattern transformation.

In the method of making a template according to the invention, the layer of single-phase polymer may be deposited on to the substrate by any conventional method such as coating, painting or spraying for example. The resulting structure is then baked at a temperature below the glass transition temperature (T$_g$) of the single-phase polymer such that a degree of instability remains in the polymer to form a firm but flexible film on top of the substrate. If a baking temperature of higher than the T$_g$ of the polymer is employed, no instability remains in the polymer. If the single-phase polymer is PMGI, which has a T$_g$ of approximately 200°C, a temperature of less than 200°C will therefore typically be employed. Preferably the temperature of this baking step is in the range 120-200°C.

A semiconductor layer may also be deposited on to the single-phase polymer layer. In this embodiment of the method according to the invention, the semiconductor layer may be deposited on to the polymer layer by any conventional method such as sputtering. The semiconductor layer is preferably applied to a structure comprising a substrate coated with a single-phase polymer layer which has preferably already been subjected to a baking step at a temperature of below the T$_g$ of the polymer. Following deposition of the semiconductor layer on to the polymer layer of such a structure, the resulting three-layer structure is then subjected to a further baking step again at a temperature of below the T$_g$ of the polymer layer.

A surface of the polymer layer is textured via induction of stress into the polymer layer. The stress induced in the polymer is typically in the range 0.5-1 MPa.

The nature of the texture or pattern so-produced is highly dependent on the applied stress, which can be applied such that highly organised and complicated patterns are achieved. For example, if a tensile or compressive strength is applied, a lined pattern in the direction of the stress will be generated in the surface of the polymer layer. Preferably, stress-induction in the polymer layer

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results in the formation of parallel grooves in the surface of the polymer layer. These parallel grooves are created because, under stress, the formation of waves with a vector in the stress direction becomes energetically unfavourable

5   thus producing periodically ordered structures in the surface of the polymer layer. This idea is analogous to pulling a wrinkled table cloth in opposite directions. The polymer film thus provides a uniform striped pattern with a characteristic wavelength (λ) as the instability in the

10 polymer layer is controlled by spinodal dewetting, ie. the dewetted wave structure is characterised by a single wavelength.

One way in which stress may be induced in the polymer layer is via the use of a load bearing member comprising at

15 least one contact surface which engages the surface to be textured. The load bearing member employed in this embodiment of the method of the invention may comprise polydimethylsiloxane (PDMS), and typically has the shape of a truncated prism. The contact surface of the load bearing

20 member may be smooth or may itself be textured.

The template of the invention is employed in the manufacture of structures on the nanometre scale, which are typically made from materials such as metals, alloys, ceramics and polymers.

25 The structures so-produced may include arrays, grids, electronic devices and optical devices, such as polarisers. Of particular interest are magnetic wire arrays, such as those comprising Permalloy ($Ni_{80}Fe_{20}$) which may be used in device applications.

30 The present invention will now be described with reference to the following examples and to the accompanying drawings. In the drawings:

Figure 1 is a side perspective view illustrating the stress-induction step of the method of making a template

35 according to the present invention, including an enlarged detail of a textured surface of the template of the invention;

Figure 2 shows atomic force microscope (ASM) images of
(A) a randomly textured surface taken from a 150 nm
thickness PMGI film following baking at 160°C, and (B) an
ordered surface resulting from stress-induction in a 250 nm
5   thickness PMGI film following baking at 160°C;

Figure 3 illustrates surface patterns induced by
localised stress and the analysis thereof. (A) shows a
surface structure obtained by pressing a sample surface
using a PDMS load bearing member which is patterned with 20
10   μm square anti-dot patterns; (B) is a schematic
illustration of the local stress distribution in sample A
in which, for simplicity, only important stress components,
τ are shown; (C) shows a defect-induced structure ordering;
(D) illustrates the distance dependence of the wavelength
15   in the vicinity of the defect;

Figure 4 shows modulated wire patterns obtained by
surface wave interference, as follows: (A) a uniform
pattern (Φ_1) aligned at 160°C;   (B) a double-line
pattern observed after heating sample with structure
20   shown in (A) for 10 min at 205°C; and (C) a single/double-
line modulated pattern obtained after heating the sample
shown in (A) to 190°C for 10 min.

Figure 5 shows scanning electron miscroscopy (SEM)
images of the fabricated structures and magnetization
25   reversal measurement of the superalloy wires, as
follows:(A) and (B) are two PMGI polymer structures (random
and aligned, respectively) defined by sequential plasma
etching, in which nanochannels were etched to the silicon
substrate; (C) shows a Permalloy wire array obtained by
30   lift-off;   (D) illustrates magnetic hysterisis loops
measured on 400 nm width and 30 nm thick Permalloy wire
arrays, in which loop 1 was taken from an unpatterned film
and loops 2 and 3 were taken when the magnetic field was
applied along and perpendicular to the wire axis
35   respectively.

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Example 1: Formation of a template using a load member with
a smooth contact surface.

250nm and 150nm thick layers of PMGI (Micro Chem
Corp., PMGI SF6) were spin-coated separately on to silicon
5   substrates and baked at 170°C for 30 min. Then 10nm-
thick germanium was deposited on to the PMGI layers by
sputtering. Random wave patterns were observed when
heating the samples above 130°C, which is well below the T_g
of pure PMGI (approximately 200°C).

10   A PDMS elastic truncated prism with a smooth contact
surface was pressed on to each sample surface as shown in
Figure 1. This Figure shows that when pressure was
applied to the PDMS prism, the intended lateral expansion
of the PDMS prism generated a stress along the film plane
15   and rendered the assembled surface structure ordered (panel
O), while on the free sample surface random wave patterns
were formed (panel R).

The atomic force microscope (AFM) images of the two
sample surfaces after heating at 160°C for 25 min are shown
20   in Figure 2. Figure 2A shows a 150 nm thickness film with
a free surface, which comprises random waves, while in the
case of an applied load to the 250 nm thickness film, the
waves are well ordered as shown in Figure 2B. The area of
the ordered structure can extend over the whole sample
25   (centimetre scale) with millimetre size domains induced by
non-uniform deformation of the PDMS prism.

In this example, the applied load was 0.5-1 MPa. A
similar order of lateral expansion stress within the
sample surface is expected because of the high Poisson's
30   ratio of the PDMS. The mechanism of wave formation is
based on the stress assisted dewetting of the polymer film
involved, which is fundamentally different from those of
other observed wave structures, such as mechanical
compression induced surface buckles. After removal of the
35   applied load the sample was annealed at 160°C for ten hours
and the ordered structure remained stable.

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Example 2: Formation of a template using a load member with a patterned contact surface.

A load member comprising a patterned contact surface was formed by casting PDMS against a 1.5 μm thick patterned photoresist layer. The resulting PDMS structure was cut into a rectangular shape to provide a PDMS load member patterned with a 20 μm square anti-dot pattern.

This member was pressed into a germanium-capped PMGI film at 160°C for 25 min. As the PMGI film was elastic, there were clear traces of the PDMS patterns printed on the sample surfaces, as indicated by the letter P in Figure 3A. In addition to these patterns, a new set of square patterns (as indicated by P′) was formed, which appeared as a copy of the initial PDMS pattern.

This additional formed patterning may be explained as follows. When the PDMS was compressed on the sample surface, the regions between holes started to expand as shown in Fig. 3B. The five typical expanding parts (the centre and four arms of a cross as indicated) generated a compressive strain in a square-framed region thus aligning the patterns along the frame. The asymmetry of the alignment of ripples is attributed to the existence of an off-normal force applied to the PDMS, which generates a tension along the horizontal direction, as shown by the open arrow in Figure 3B.

In general, the value of applied stress is expected to be much smaller than the internal stress of a film, which is responsible for the film instability. The external stress is used merely to suppress the structural disorder induced by thermal fluctuation and to align the wavelike patterns. The internal stress, which causes film instability, is accumulated due to the temperature rise during annealing and can be expressed as:

$$\sigma_0 = \int_{T_0}^{T} \frac{E_c}{1 - \nu_c} (\alpha_p - \alpha_c) dT \qquad (1)$$

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where T_0 and T are, respectively, the stress free
temperature and the temperature to which the film is
heated, E_c is the Young's modulus and v_c the Poission's
ratio of the germanium film, and α_c (α_p) is the thermal
5   expansion coefficient of the polymer film. For a PMGI
film without a germanium capping layer no instability is
found and the substrate effect can therefore be
neglected. It is difficult to calculate the value of σ_0
precisely since the value of α_p depends strongly on the
10 temperature and an additional polymerized layer could
form at the interface between the polymer and the capping
(germanium) layers. However, a reasonable estimate
gives σ_0 of approximately 100 MPa, based on
$E_c / (1-v_c) \sim 10^{11}$Pa and $(\alpha_p - \alpha_c)(T-T_o) \sim 10^{-3}$. This is about two
15 orders higher than the applied stress. Thus, the applied
stress only acts as a small perturbation to the isotropic
internal stress σ_0 and introduces an anisotropy which
leads the structure to order.

        This can be further understood through the
20 examination of the ordering of a local structure
generated by a defect centre. Figure 3C shows a typical
structure at the vicinity of a defect on a load free
sample. When a defect, for example a dust particle or
pin hole, exists in a polymer film restrained by a
25 capping (germanium) layer, the break of film continuity
leads to a redistribution of stress inside the film. By
expressing the radial and traverse components of the
stress around the defect as σ_r and σ_t, respectively, this
gives:

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$$\sigma_r = \sigma_o (1-e^{-r/\xi}), \qquad (2a)$$

$$\sigma_t = \sigma_o (1-v_c e^{-r/\xi}), \qquad (2b)$$

35 where r is the radius calculated from the edge of the
defect and ξ is a characteristic length of the stress

distribution. For stress-assisted instability in a
rubber-like polymer film, the relationship between the
surface wavelength and stress is $\lambda = K/\sigma^2$, where K is a
constant. Considering that the redistribution of
material during formation of the wavelike structure is
caused by the internal stress along the wave vector
direction, it follows that:

$$\lambda = \frac{\lambda_o}{(1 - v_c e^{-r/\xi})^2} \qquad (3)$$

where λ_0 is the wave length of the structure far away
from the defect centre. Taking $v_c = 0.4$, the
characteristic length ξ was found to be about 10 μm by
fitting equation (3) with experimental results as shown
in Figure 3D. If the radius of the whole ordered region
is taken to be 20μm (see Figure 3C), a value of the
stress anisotropy required for ordering the structures in
a sample from equation(2) may be obtained as follows:

$$a = \frac{\sigma_t - \sigma_r}{\sigma_t + \sigma_r} \sim 4\% \qquad (4)$$

This result confirms that a small perturbation in the
stress can dramatically modify the structure morphology.

Example 3: Provision of complex patterning via changes in
experimental conditions.

This Example provides another method of making a
template , the so-called "surface wave interference", to
create more complex patterns. The wavelength of surface
patterns is normally determined by the fastest growing
wave mode in the system and strongly depends on

experimental parameters. If a wave pattern $\Phi_1 = \varepsilon_1(t)e^{iq_1 x}$ is

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the characteristic mode in a given experimental condition, a rapid change of the sample condition will create a new characteristic wave $\Phi_2 = \varepsilon_2(t)e^{i(q_2 x + \varphi)}$. In the time period when the decaying wave Φ_1 and arising wave Φ_2

5   co-exist a new pattern induced by their interference is observed.

Figure 4A shows an aligned wave Φ_1 created at 160°C and Figure 4B shows a double line pattern obtained after further heating the sample for 10 min at 205°C without

10   the application of a load. This example shows that the dominant surface wavelength of the film at 205°C is about twice of that at 160°C ($q_2 \sim q_1/2$) due to strong softening of the polymer near its glass transition point. Figure 4B illustrates the pattern formed in a film which has not

15   yet reached its steady state. This may be expressed as

$$\Phi = \Phi_1 + \Phi_2 = \varepsilon_1(t)e^{iq_1 x} + \varepsilon_2(t)e^{i(q_1 x/2 + \varphi)}$$. The value of the phase

shift φ is required for pattern symmetry. Similarly, the wavelength obtained at 190 °C is about 1.7 times of that obtained at 160 °C. After heating the sample with wave

20   Φ_1 to 190 °C for 10 min a single/double line modulated structure can be found, as shown in Figure 4C, which

agrees well with $\Phi' = \Phi_1 + \Phi'_2 = \varepsilon_1(t)e^{iqx} + \varepsilon_2(t)e^{i(2q_1 x/3)}$

In order to utilise such an interference effect to create complex patterns, it would be ideal if the

25   wavelengths of both Φ_1 and Φ_2 could be chosen as desired. There is no limit to the number of the waves which may be included, and the obtained wave ($\Phi_1 + \Phi_2$) may further interfere with another wave Φ_3 to create more complex patterning, e.g. $\Phi = [(\Phi_1 + \Phi_2) + \Phi_3] + \cdots$. Desired structures

30   displaying abundant line arrangements with the appearance of bar-codes are possible. Such observed interference

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patterns and their evolution process are of use in the
fundamental study of dynamic processes of polymer
diffusion and creep, and wave mode selection due to film
instability.

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Example 4: Fabrication of a nanostructure.

        The wavelength of the lined patterns obtained in the
above-described germanium-capped PMGI template was in the
micron to submicron range, and their amplitude was around
10   20nm.

        A 40 nm thick PMMA (Micro Chem Corp. 950 PMMA A2)
resist layer was spin-coated on to the template surface
and the resulting structure was baked at 160°C for 5 min
before being cooled to room temperature. A glass wafer
15   was employed to protect the surface flatness of the PMMA
layer. After partially removing the PMMA layer by oxygen
(O_2) plasma etching, the remaining PMMA in the trenches
of the template was used as mask during etching of the
thin germanium layer by sulphur hexafluoride (SF_6).
20   Subsequently the patterned germanium layer was used as
another mask during etching through the PMGI by O_2
plasma. Finally, a layer of functional material, such as
metal, was deposited on to the structure and the desired
nanostructures were obtained by lifting off the rest of
25   the PMGI polymer.

        By varying the parameters employed in the etching of
the PMMA layer, the line width of the etched PMGI could
be controlled. Figure 5A and 5B show, respectively,
typical SEM images of random and ordered polymer
30   structures on a silicon substrate after the final
reactive ion etching (RIE). The channel width obtained
was approximately 150 nm and the whole pattern was
uniform and defect-free over a large area.

        Figure 5C shows a magnetic wire array of 30nm thick
35   Permalloy ($Ni_{80}Fe_{20}$) obtained in this way. In recent
years, such fine patterned magnetic wires have attracted
great scientific interest in particular in device

applications. The magnetization reversal of fabricated
permalloy wires were studied by the magneto-optic Kerr
effect technique and the results are shown in Figure 5D.
Compared to the unpatterned film (loop 1), the large
5   increase in the coercivity obtained with the field along
the wire (loop 2) is attributed to the shape anisotropy
induced complication of magnetization reversal, such as
the so-called "bucking effect" etc. When the field was
applied perpendicular to the wires, a remarkable increase
10   in the saturation field was observed (loop 3). This could
be explained by the "magnetic charges" induced along the
wire edges, resulting a magnetically hard behaviour in
the direction perpendicular to the wires.

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